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Sunlight-Induced Photodecomposition of Chlorine Dioxide

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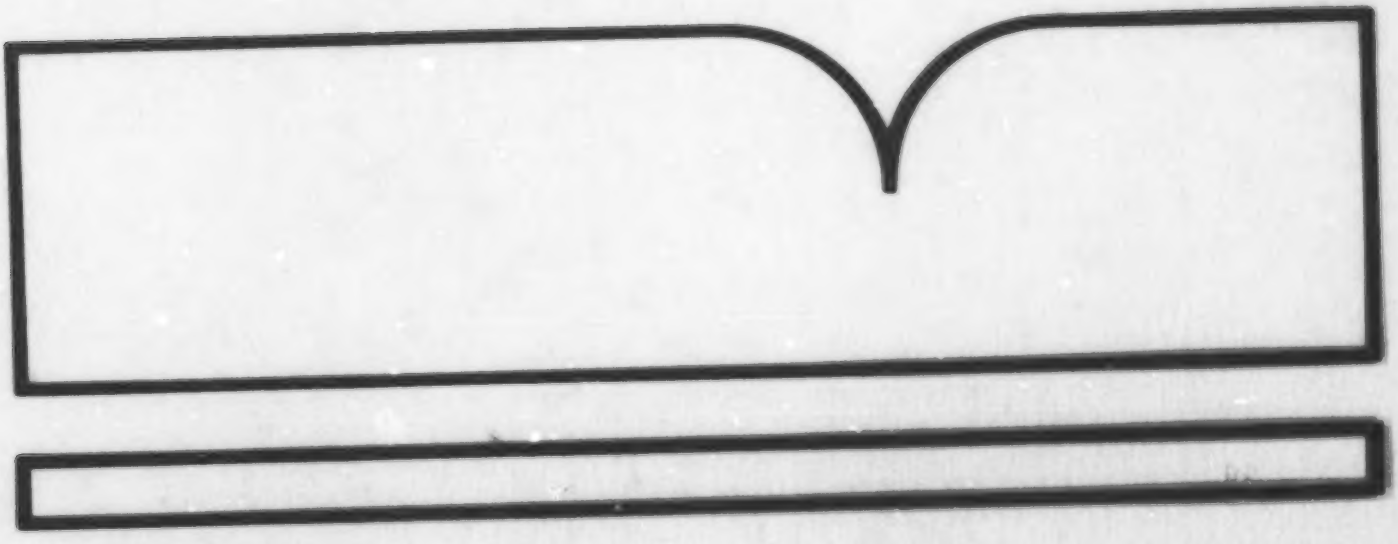

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16. ABSTRACT
At many water treatment facilities, water being treated by an oxidant is exposed to direct sunlight. The ready decomposition of both ClO_2 and ClO_2^- by sunlight and fluorescent lights can lead to significant losses during water treatment. The characteristics of the water plays an important role in the nature of the byproducts resulting from light-initiated reactions, and significant levels of ClO_3^-, BrO_3^-, and bromoform can be produced. The bromide ion was found to play a particularly important role in THM formation and in initiating light reactions that accelerated the decomposition of ClO_2 in the dark.

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CHAPTER 82

Sunlight-Induced Photodecomposition of Chlorine Dioxide

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Rod G. Zika, Cynthia A. Moore, Louis T. Gidel, and William J. Cooper

Many water treatment facilities, at some point after or immediately before addition of the oxidant, expose the water being treated to direct sunlight. Because of the significant sunlight absorption by some of the oxidants, the chemical pathway leading to their decomposition can be dramatically altered. Potentially, this can have a pronounced effect on the nature of the inorganic by-products of the oxidant decomposition and on the halogenated organic materials produced via interaction with the oxidant photoproducts. In sunlight, direct photolytic decomposition will only be significant for those oxidants that exhibit appreciable light absorption at wavelengths longer than 300 nm. Of all the water treatment oxidants, ClO_2 is most prone to photochemical decomposition during sunlight exposure. This is because of its high light absorption in the near-UV and visible region of the spectrum and high quantum yields, reported to be 1.0 mol/Einstein at 405 nm and lower wavelengths.

The gas-phase photochemistry of ClO_2 has been studied extensively.[1-4] However, far less attention has been paid to its photolysis in aqueous solution.[5-8] In the gas phase, the primary photochemcial reaction is the homolytic fission of the chlorine oxygen bond:

$$ClO_2 \rightarrow ClO + O \qquad (1)$$

The products of this primary reaction then go on to generate secondary products such as chlorine peroxide (ClOO), excited state oxygen (O_2^*), chlorine (Cl_2), chlorine trioxide (Cl_2O_3), chlorine hexoxide (Cl_2O_6), and the recently proposed chlorine perchlorate ($ClOClO_3$).[9]

In aqueous solution, the primary photoreaction product ClO is not observed, and O appears to be a minor product since little O_3 is found in oxygenated aqueous solutions.[8] It is postulated that the reaction proceeds, as in the gas phase, to give ClO and O, but these products then undergo solvent cage recombination to generate chlorine atoms and molecular oxygen. In addition, a rapid bulk solution reaction between ClO and ClO_2 produces Cl_2O_3, and the reaction between Cl (or Cl_2^-) and ClO_2 leads to Cl_2O_2. Rapid hydrolysis of Cl_2O_3 and Cl_2O_2 leads to the formation of the observed products ClO_3^-, ClO_2^- and Cl^-. The overall reaction is as follows:

$$ClO_2 \rightarrow (ClO + O)\ \text{cage} \quad (2)$$

$$(ClO + O)\ \text{cage} \rightarrow Cl + O_2 \quad (3)$$

$$ClO + ClO_2 \rightarrow Cl_2O_3 \quad (4)$$

$$Cl_2O_3 + H_2O \rightarrow ClO^- + ClO_3^- + 2H^+ \quad (5)$$

$$Cl + Cl^- \rightarrow Cl_2^- \quad (6)$$

$$Cl\ (\text{or } Cl_2^-) + ClO_2 \rightarrow Cl_2O_2 \quad (7)$$

$$Cl_2O_2 + H_2O \rightarrow Cl^- + ClO_3^- + 2H^+ \quad (8)$$

$$O + O_2 \rightarrow O_3 \quad (9)$$

Interestingly, although ClO_2 has the distinct advantage in water treatment of not having the capacity to oxidize Br^-, many of its transient photolysis products do. The appearance of transitory species during the flash photolysis of ClO_2 solutions, which contained low levels of Br^-, have been reported.[8] The transients are believed to be Br_2^- or $BrCl^-$. The information on the reactions of these radicals with organic compounds is scarce; however, it has been shown that they do react at appreciable rates with alcohols.[9] By analogy with the Cl_2^- radical, bromine radical anions should undergo addition to alkenes and aromatic compounds.

In this chapter, the light-induced decomposition of ClO_2 is examined in an attempt to characterize inorganic products and trihalomethane (THM) formation, and to describe the extent to which sunlight-induced photodecomposition might occur during water treatment.

EXPERIMENTAL

Chlorine dioxide used in this study was prepared from sodium chlorite (80% purity) obtained from Alfa Products and potassium persulfate (reagent grade) obtained from Mallinckrodt. A standard procedure was used to prepare and handle the ClO_2.[10] Stock solutions thus prepared were stored refrigerated and protected from light. They were standardized immediately before being used in experiments.

Chlorine dioxide solutions for sunlight reaction studies were prepared by adding the concentrated stock solution to organic-demand-free water in 10-cm quartz spectrophotometer cells. The cells were sealed so that no headspace existed. The initial concentration was calculated from the measured absorbance at 360 nm using a molar extinction coefficient, Σ, of 1035 L mol^{-1} cm^{-1}. Sunlight exposure experiments were conducted on the roof of the laboratory. The integrated solar flux during the experiments was determined with an Eppley Laboratory Ultraviolet Radiometer, Model TUVR. Changes in the ClO_2 and light absorbing product concentrations during the course of the experiments were determined from the UV-vis spectra. Controls were run

simultaneously by storing sample cells in the dark at the same temperature as the light-exposed samples. Experiments involving fluorescent room lighting were conducted in a similar manner. The samples were exposed to standard laboratory fluorescent lights on a bench ~7 ft below overhead light fixtures.

Quantum yield studies were conducted using a Kratos/Schoeffel 1000-W mercury-xenon monochromatic irradiation system. Quantum yields were determined at the mercury lines 296.7, 313.0, 334.1, 366, 404.5, and 435.8 nm, with a bandwidth of ~7 nm. The intensity at each line was determined using ferrioxalate actinometry.[11] The measurements were performed in 10-cm quartz spectrophotometry cells in the same way as described for the sunlight experiments. Time intervals for light exposure varied (i.e., 10 to 120 s) and were optimized to examine the reaction during the first 10% of the decay curve.

Natural water samples were placed in 60-mL reaction vials, spiked with ClO_2 at $\sim 1.5 \times 10^{-4} M$ (10 mg/L), topped with additional water, and capped with Teflon-lined septa. The vials were then either placed in the dark as controls or exposed to sunlight on the roof. The sunlight was monitored with the Eppley Radiometer, and the samples were exposed for a period in excess of twice the half-life for ClO_2^- (a product of ClO_2 photodecomposition) photolysis. This interval was usually about 4 h at midday. The dark- and light-exposed samples were then quenched by adding a slight excess of sodium thiosulfate. The capped samples were refrigerated and analyzed by gas chromatography for THMs.[12] Samples for anion analysis were prepared by purging residual ClO_2 with N_2 gas to quench the reaction. Analyses were conducted using ion chromatography on a Dionex Model 10 chromatograph with a "fast anion" column and 0.0015 M Na_2CO_3 as eluant. The column flow rate was 3.0 mL/min. With these conditions, the approximate retention times in minutes for anions were ClO_2^- at 2.40; BrO_3^- at 3.10; Cl^- at 3.45; Br^- at 8.10; and ClO_3^- at 9.25.

RESULTS AND DISCUSSION

Sunlight Studies

Aqueous solutions of ClO_2 in sealed 10-cm spectrophotometer cells were exposed to summer midday solar radiation. The resultant photochemical decay of ClO_2 is shown in Figure 1. The results indicate that ClO_2 should have a lifetime of <0.5 min in water exposed to bright sunlight. To evaluate the wavelength dependence of the reaction, quantum yields for the decomposition of ClO_2 were measured at various wavelengths. The quantum yields were compared with those determined earlier (Table I) by Bowen and Cheung.[5] The reasons for the differences in quantum yields determined in the two studies are not apparent but could be the result of the differences in methodologies. There is, for instance, no information in the Bowen and Cheung report on the pH of the reaction solutions. Although differences between pH 7.0 and 9.0 appear to be negligible, it is possible that the spread could be significantly larger at more-

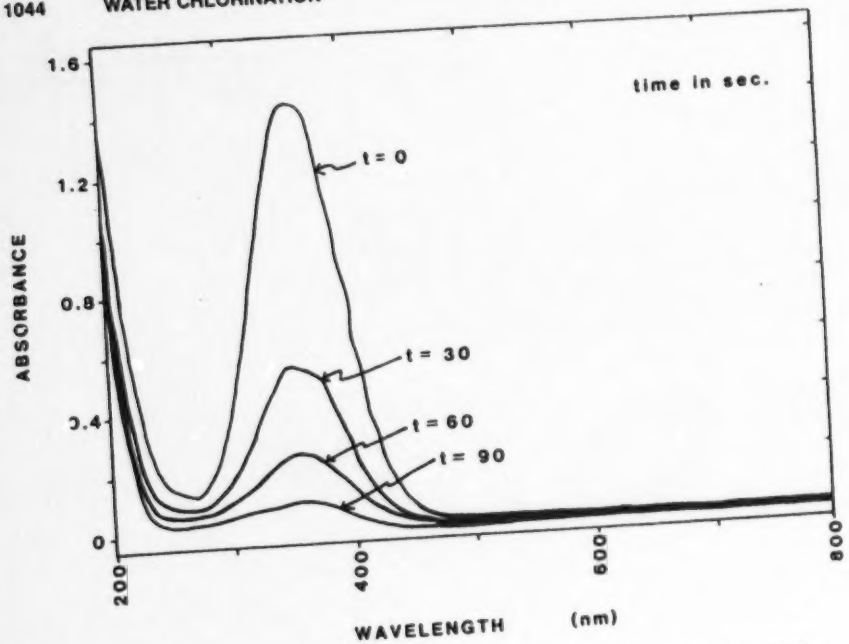

Figure 1. Photochemical decomposition of chlorine dioxide aqueous solution in sunlight.

Table I. Decomposition Quantum Yields (Φ) of ClO_2

Wavelength (nm)	From Bowen and Cheung[5]	This Work at pH	
		7.0	9.0
296.7	1.00	1.40 ± 0.03	1.47 ± 0.09
300		0.98 ± 0.02	0.86 ± 0.01
313.0		0.90 ± 0.02	0.90 ± 0.02
334.1	0.76	0.46 ± 0.02	0.46 ± 0.02
366.0	0.51	0.13 ± 0.02	
404.5	0.21		
435.8			

acidic pH values. In water treatment applications, however, pH values in the 7 to 9 range are more likely to be encountered in ClO_2 treatment applications.

Another complication in comparing the results is caused by the possible differences in the bandwidth of the incident radiation. In the work presented here, a high-energy monochromator with a bandwidth of less than 7 nm was used to isolate mercury lines. It is clear from the Bowen and Cheung report

that for the 300-nm value of $\Phi = 1.00$, a broad spectral region of 316 to 270 nm was used. The rapidly changing values of Φ and ClO_2 absorbance in this region make it unlikely that the quantum yields from the two studies would agree closely. This same problem could contribute to the lack of agreement at other wavelengths. Unfortunately, the filter combinations used in the Bowen and Cheung report to isolate other mercury lines could not be reproduced in our laboratory because the glass filters used are apparently no longer available.

Reaction Products

When ClO_2 is used as an oxidant in water treatment applications, the resultant thermal and photochemical decomposition pathways become considerably more complex than they are in pure water solutions of ClO_2. Compositional variations in the particular water can have a pronounced effect on the mechanism and the products generated. The occurrence of oxidizable substrates in the water will contribute to the amount of ClO_2^- produced from ClO_2 via dark oxidation reactions. The photochemical decomposition of ClO_2 will then also involve ClO_2^-, which has a moderately strong electronic absorption spectra in the near-UV region of sunlight. The complex nature of the mechanism can be observed from the changing electronic absorption spectra of ClO_2^- solutions during sunlight exposure (Figure 2). It is obvious that ClO_2^- has a lifetime of < 10 min in full sunlight and that its reaction products are ClO_2 and OCl^-. The photochemistry of ClO_2^- has been extensively covered elsewhere[13,14] and will not be further discussed here. It is worth noting, however, that the photochemistry of ClO_2 in disinfection application will to some extent, depending on the characteristics of the water and the light-spectral distribution, involve the oxidants ClO_2, ClO_2^- and OCl^-.

The major stable end products of ClO_2 photolysis in aqueous solution are Cl^-, ClO_3^- and O_2.[5] The Cl^- and ClO_3^- are produced through hydrolysis of Cl_2O_3 and Cl_2O_2, with ClO^- and Cl also involved in the reaction sequence.[2-8] An advantage of ClO_2 in disinfection is its inability to oxidize Br^-; however, in solution exposed to light, these intermediate oxidants could initiate reactions such as

$$OCl^- + Br^- \rightarrow OBr^- + Cl^- \quad (10)$$

$$Cl + Br^- \rightarrow ClBr^- \quad (11)$$

In solutions of $1.5 \times 10^{-4} M$ ClO_2, which were exposed to direct sunlight, ion chromatographic analysis revealed that the only major ionic products were Cl^- and ClO_3^-. When 1×10^{-4} M Br^- was added to the solution, BrO_3^- was also observed as a product (Figure 3). Although the ClO_2 was photolyzed during the first few minutes of the reaction, the BrO_3^- gradually increased on contin-

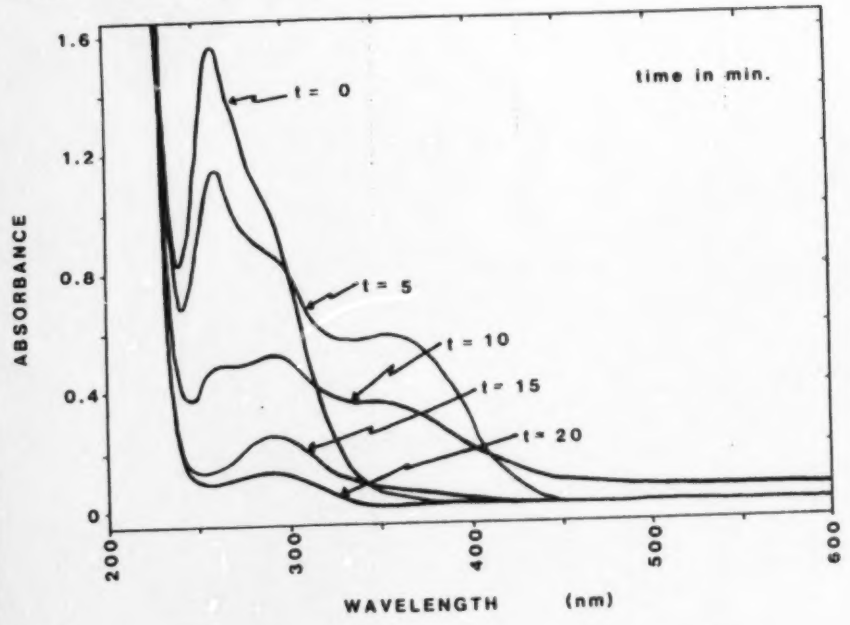

Figure 2. Photochemical decomposition of chlorite aqueous solution in sunlight.

ued exposure to sunlight. The amount of Br^- concentration decreased initially to 50% of that added and then increased as the reaction proceeded. This is interpreted as an initial rapid oxidation of Br^- to $OBr,^-$ which then reacts photochemically[15]

$$3\ OBr^- \rightarrow BrO_3^- + 2\ Br^- \qquad (12)$$

to generate the observed product distributions. The OBr^- would not be detected using the ion chromatographic determination as described previously.

In water containing significant amounts of labile organic materials, the organic product yields might vary because of available organic scavengers. When ClO_2 was added to groundwater and exposed to sunlight, THM analysis revealed a linear increase in bromoform formation with increasing Br^- concentration (Figure 4). The onset of significant $CHBr_3$ formation in this water appears at about 1 mg/L Br^-. A low yield of $CHCl_3$ was also observed which, within the limits of analytical precision, appeared to be independent of Br^- concentration.

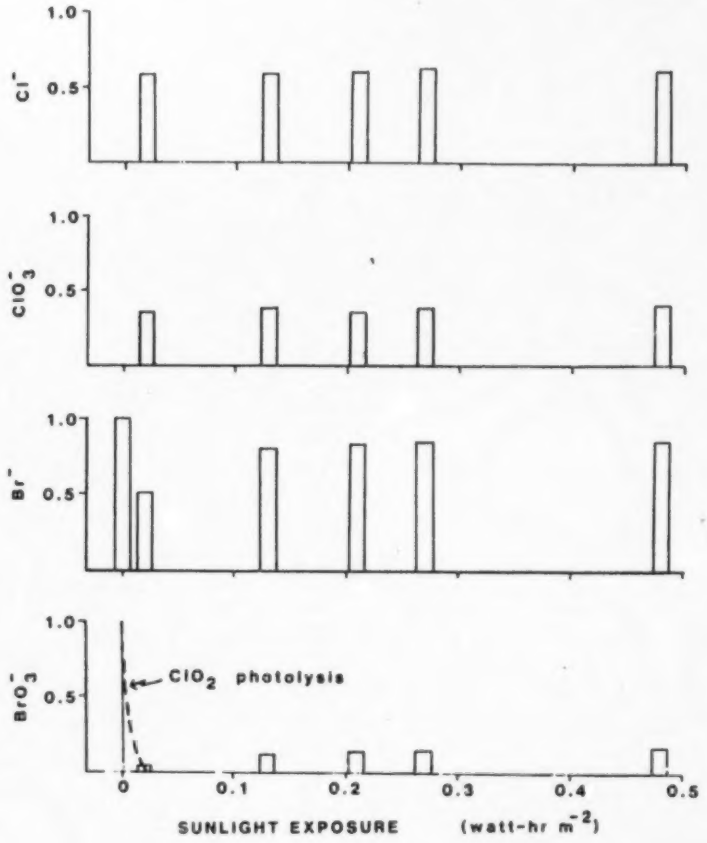

Figure 3. Major anionic products of ClO_2 photolysis in solutions containing 1×10^{-4} *M* Br^- and 1×10^{-4} *M* ClO_2 at pH 7.0. Vertical axes represent relative molar concentration.

To examine the effect of natural water composition on $CHBr_3$ formation, water from three different wells in the South Florida area was enriched with Br^-, dosed with $1.5 \times 10^{-4}M$ ClO_2, and exposed to sunlight. The yields of $CHBr_3$ are shown in Table II for pH 5, 7, and 9. The highest yields were observed for all water samples at pH 5, which is not consistent with the usual trend of increasing THM production with increasing pH. This decreasing yield could be due to an increased photolysis decomposition rate of the active bromine species at elevated pH.[16] There is the added complication that water composition also affects the $CHBr_3$ production, as is indicated for the Orr well 2 sample, which displayed less pH dependence than the other two wellwater

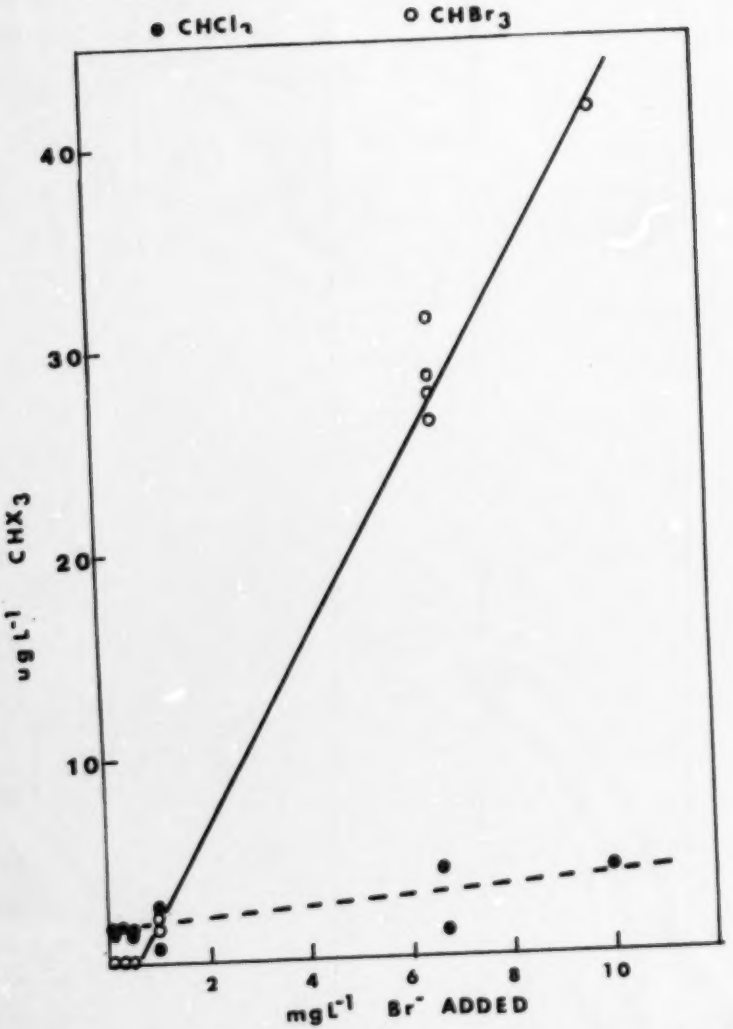

Figure 4. Effect of Br^- concentration on THM formation when groundwater samples, to which 1×10^{-4} *M* ClO_2 has been added, are exposed to sunlight.

samples. There is no direct correlation to organic carbon content, since Preston well 5 and Northwest well 3 had approximately the same level of total organic carbon (i.e., 6.3 mg/L) but very different concentrations of $CHBr_3$. The Orr well was comparable to the Preston well in $CHBr_3$ production at pH 5, but had only 2.2 mg/L TOC. The extent to which halogen radicals (i.e., Cl_2^-, Br_2^-, $ClBr^-$) are involved in THM formation is unknown. If, however, they are involved, then composition factors such as the concentration of inorganic anions may play an important role. High levels of HCO_3^- or CO_3^{2-} would rapidly quench active halogen radicals, thereby limiting $CHBr_3$ production.

Table II. Bromoform Formation from ClO_2 (μg/L)

	pH 5		pH 7		pH 9	
Source of Water	Light	Dark	Light	Dark	Light	Dark
Preston well 5	50	ND[a]	7	ND	0	ND
Orr well 2	44	ND	21	ND	17	
Northwest well 3	13	ND	ND	ND	ND	ND

[a]Not determined.

Another interesting facet of Br^- involvement in ClO_2 photolysis is shown in Figures 5 and 6. In these experiments, 1.5×10^{-4}*M* ClO_2 solutions containing 1×10^{-4}*M* Br^- were exposed to alternating 12-h light and dark periods. Irradiation during the light periods was supplied by overhead fluorescent room lights. It is apparent from Figure 5 that without added Br^-, no significant ClO_2 decay occurred during the dark periods. When Br^- was present, however, the initial light exposure period apparently generated photoproducts that enhanced the ClO_2 decay reaction during subsequent dark and light exposure periods.

In summary, the nature of the compositional variations that affect ClO_2 decomposition and $CHBr_3$ formation are still obscure, and the reaction mechanisms are complex.

PHOTOCHEMICAL DECOMPOSITION MODELING

The photolysis rate and half-life of ClO_2 were calculated for waters with organic contents of 0.53, 6.20, and 17.6 mg/L TOC using a modified version of the photochemical model of Zepp and Cline.[17] The photolysis rate is calculated based on the assumption that the loss occurs as a result of primary processes. Any secondary reactions that may lead to a loss of ClO_2 would lead to a faster rate. This model calculates the attenuation of light in the water column resulting from absorption and Rayleigh scattering within the water column itself and from the layer average amount of light absorbed between the surface and a depth D. Solar fluxes at ground level are specified as a function of time of day, season, total ozone column amounts, and the latitude based on the regression analysis of Benner.[18] Other critical input parameters are water absorbance, molar extinction coefficient, and quantum yield, all as a function of wavelength. Except for surface photolysis rates, all other calculated rates represent averages over the depth of shallow holding ponds with weak thermal stratification and sufficiently strong wind. Thermally or mechanically driven mixing cycles the water from the bottom to the surface on a time scale faster

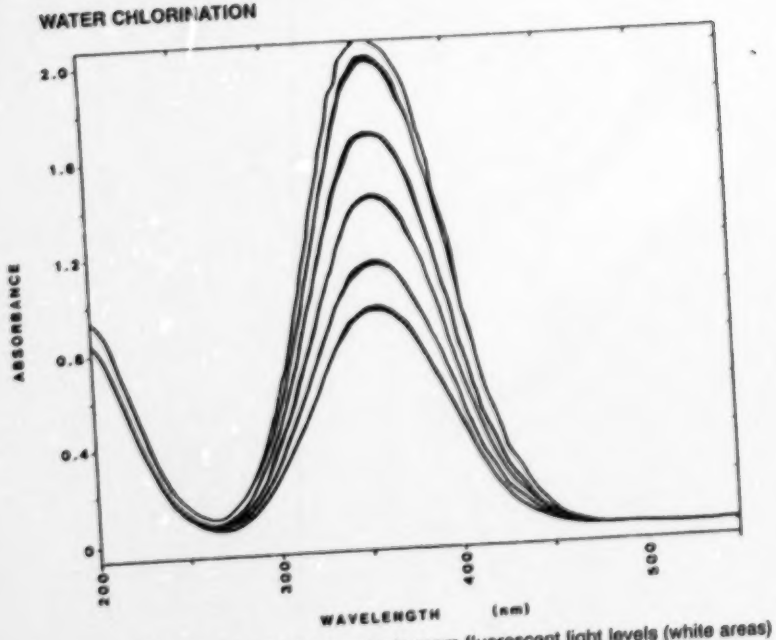

Figure 5. Alternating 12-h periods of exposure to room fluorescent light levels (white areas) and to the dark (shaded areas). Initial concentration of ClO_2, 1×10^{-4} *M*.

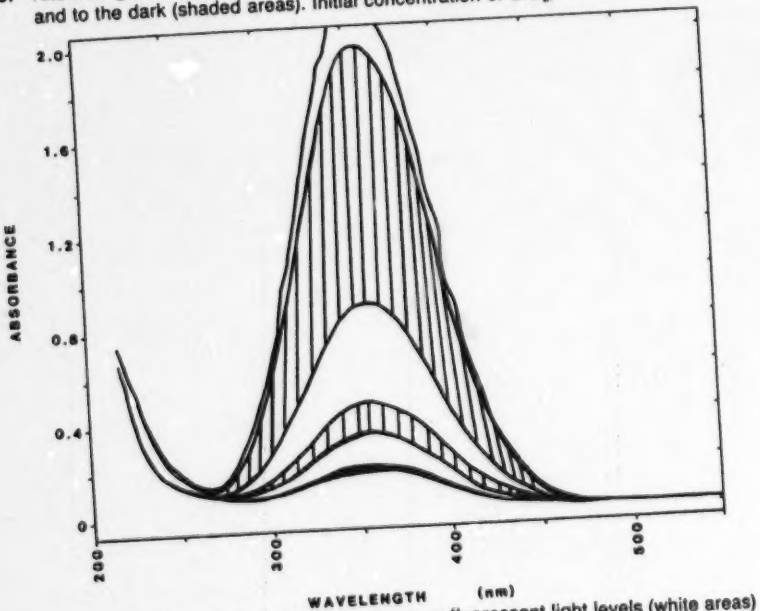

Figure 6. Alternating 12-h periods of exposure to room fluorescent light levels (white areas) and to the dark (shaded areas). Initial concentration of ClO_2, 1×10^{-4} *M* with 1×10^{-4} *M* of Br^- present.

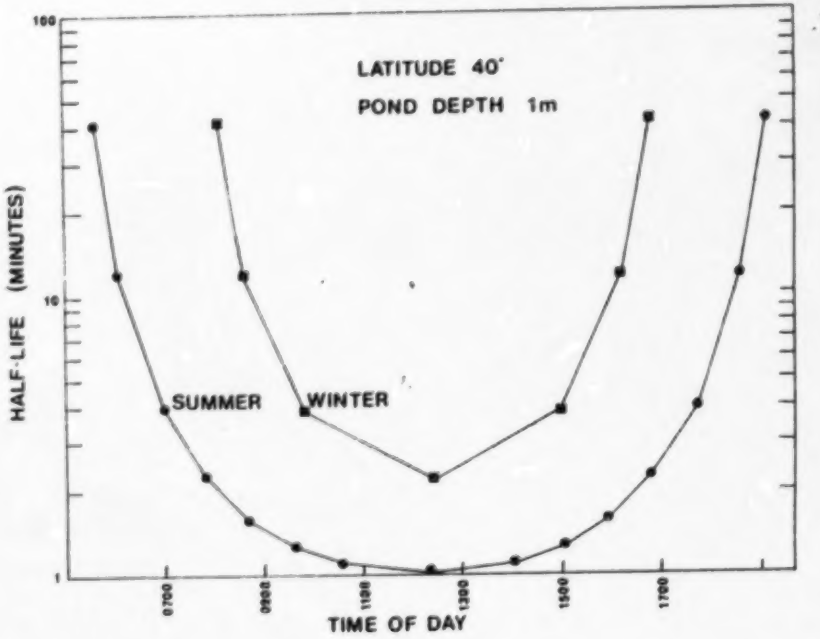

Figure 7. Time-of-day variation in half-life of ClO_2 for sunlight exposure for midsummer and midwinter in contact pond water with a depth of 1 m.

than the half-life because of photolysis, so that photolysis rather than mixing is the rate-limiting step in the destruction of ClO_2. As the photolysis rate increases, the assumption is no longer valid; the calculated half-life is then only a lower limit, with mixing in the pond becoming the rate-limiting step in the loss process.

The time-of-day variation in the half-life for a 1-m-deep pond at 40° latitude in winter and summer is shown in Figure 7. At midday in summer, the lifetime is about 1 min and is always <10 min during the daylight hours. In winter, photolysis is only important during the middle 6 h of the day. Figure 8 shows the variation of the half-life with the depth of the holding pond for waters of different clarities ranging from clear to dark-colored (i.e., 17.6 mg/L). For clear water (i.e., 0.53 mg/L), the half-life is nowhere as sensitive to the depth of the pond as for colored water. In 17.6 mg/L, most of the light is absorbed in the upper 10 cm; therefore, the loss rate will be dependent on the strength of the mixing.

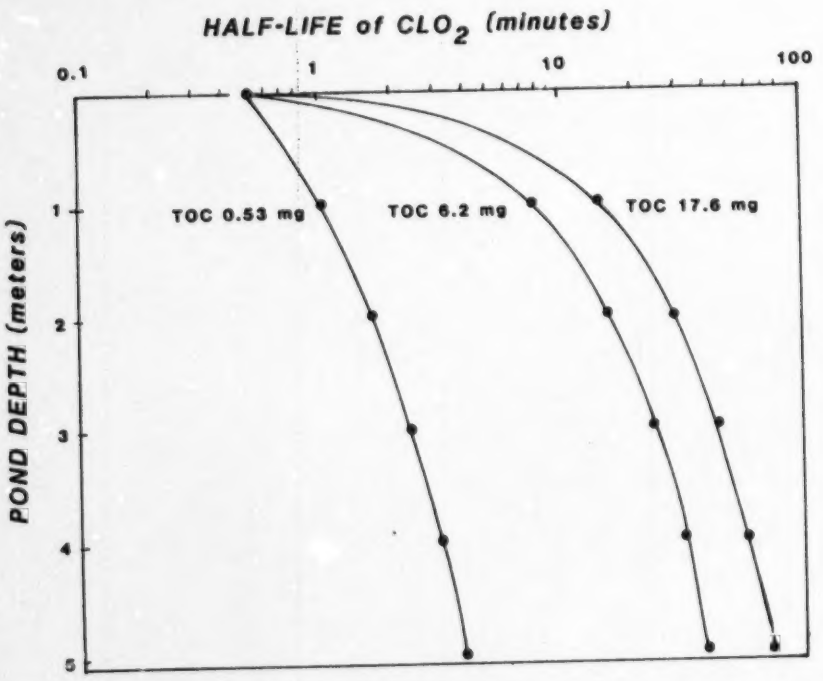

Figure 8. Variations of half-life of ClO_2 in ponds of different depths and with different total organic carbon concentrations when exposed to sunlight at 40° latitude in midsummer.

CONCLUSIONS

Both ClO_2 and ClO_2^- are readily decomposed by sunlight and fluorescent lights. This can lead to significant losses during water treatment. The characteristics of the water play an important role in the nature of products resulting from light-initiated reactions. Significant levels of ClO_3^-, BrO_3^-, and bromoform can be produced. The bromide ion was found to play a particularly important role in THM formation and in initiating light reactions that accelerated the decomposition of ClO_2 in the dark.

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